



WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: Arsenic Remediation of Drinking Water

Focus Categories: TRT, TS, WQL

Keywords: Adsorption and Exchange, Arsenic, Geochemistry, Ground-Water Quality, Water Chemistry, Water Quality, Water Quality Standards, Water Treatment

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Congressional District: First

Statement of Critical Regional or State Water Problems

Arsenic retention and mobility in surface water and ground water are of great concern because of toxic effects on the environment. The drinking water standard for arsenic, currently set at 50 parts per billion (ppb), is likely to be lowered in the next year because of links to cancer. Current remediation technologies are quite expensive. Thus, any lowering of the standard will put increased economic pressure on rural communities with high levels of arsenic in their drinking water. The American Water Works Association has estimated the cost of decreasing the arsenic standard to 10 ppb in South Dakota at \$8.25 million.

Statement of Results or Benefits

The proposed research will investigate the feasibility of developing a low-cost remediation technology for removal of arsenic from surface water and ground water. Arsenic retention and transport will be characterized. Because of the ready availability of limestone, its use for arsenic remediation would be relatively inexpensive. If successful, it is anticipated that the technology could be readily adapted to small rural water supply systems as well as private, domestic, and stock wells. For example, elevated levels of

arsenic in water from wells in the Arikaree aquifer have been observed on the Rosebud Indian Reservation. However, observations of arsenic contamination from mining and native mineral sources in the northern Black Hills indicate that arsenic appears to be retained by the karstic Madison Limestone aquifer. Benefits of this research will include a low-cost treatment technology that reduces arsenic below maximum contaminant levels, helping operators of small or rural water supply systems to meet anticipated new rules.

Nature, Scope, and Objectives of the Research

The specific objectives of this work are to: (1) establish the maximum capacity of limestone to retain arsenic, (2) determine the effect of pH and surface area on the adsorption efficiency, and (3) compare arsenic retention on limestone with other materials such as Arikaree sandstone and pure CaCO_3 . Preliminary work that has recently been completed by the principal investigators demonstrates arsenic adsorption of greater than 90% by limestone.

This proposed research is part of a larger program of arsenic-related work that the principal investigators have undertaken during the past year. The overall vision and scope are to understand the physical and geochemical processes that govern arsenic retention and transport in ground water, with emphasis on adsorption by limestone. Results will be complemented by examination of arsenic transport in ground water and surface water in the region of the Arikaree aquifer on the Rosebud Indian Reservation. Finally, the guiding purpose of the program is to develop a low-cost remediation technology for arsenic removal that can be easily adapted to rural supply systems. The specific research in this proposal will advance our understanding of the maximum adsorptive capacity of limestone and the pH dependence of the process.

Introduction and Objectives

Arsenic retention and mobility in surface water and ground water are of great concern because of their toxic effects in the environment. The drinking water standard for arsenic, currently set at 50 ppb, is likely to be lowered in the next year because of links to cancer. Current remediation technologies are quite expensive. Thus, any lowering of the standard will put increased economic pressure on rural communities with high levels of arsenic in their drinking water (Frey et al., 1998).

Arsenic, at pH 8 and above, is readily soluble and thus transports easily through ground water. However, observations of arsenic contamination from mining and native mineral sources in the northern Black Hills indicate that arsenic appears to be retained by the karstic Madison Limestone aquifer. This could be a result of adsorption or precipitation on the limestone and dolomite mineral surfaces. Preliminary column tests using crushed Madison Limestone as the bed material indicated significant retention of arsenic (Webb and Davis, 1999). Because of the ready availability of limestone, the proposed research will investigate the feasibility of developing a low-cost remediation technology for removal of arsenic from surface water and ground water.

Arsenic in the aquatic environment has very complex chemistry that is dependent on a number of factors, including pH and redox potential. Measurement of arsenic contamination has been limited, until very recently, to analysis of concentrations. Unfortunately, it is the speciation of a chemical substance that governs its availability, accumulation, and toxicity to living organisms as well as its mobility in the environment. This is particularly important for arsenic, whose arsenite form, As(III), is much more toxic than arsenate, As(V). While As(V) is considered to be the less toxic form and is also the most stable form in oxidized environments, significant amounts of As(III) can exist in oxidizing environments (Seyler and Marin, 1989). The distribution between arsenate and arsenite is also highly sensitive to the redox potential. At more oxidizing conditions, arsenate tends to be dominant. The solubility of these species depends on a number of factors including pH, cations present, and adsorbing surfaces.

Under certain conditions, the solubility and adsorption appears to be controlled by the presence of iron, manganese and their respective oxides (Driehaus et al., 1995). Surface adsorption of arsenic to iron hydroxide and clay minerals has been extensively characterized (Manning and Goldberg, 1997; Grossl et al., 1997; Pierce and Moore, 1982; Goldberg, 1986; McNeill and Edwards, 1997; Raven et al., 1998). At pH 8, arsenite has a much lower potential for adsorption on oxides or clay edges, than arsenate, which exhibits strong adsorptive potential from a range of pH 3 to pH 11. At oxidizing conditions, Fe(III)-arsenate compounds are stable. Under reducing conditions, Fe(III) is converted to Fe(II) and arsenate to arsenite, significantly increasing the solubility of arsenic at pH 8. Even though a knowledge of speciation is essential in predicting the environmental impacts, the speciation of chemicals in the environment and their transformations with time are, at best, poorly understood (Mariner et al., 1996; Edwards et al., 1998, Manning and Marens, 1997). As(V) is also the form that is more readily co-precipitated with or absorbed on metal oxides. Investigation of the speciation of arsenic and its influence on the mobility and retention of arsenic will be established as part of the larger research program.

The influence of natural aquifer material on arsenic transport, speciation, and retention has been the subject of recent investigations. Mariner et al. (1996) examined the effects of high pH on arsenic mobility in a sandy aquifer in the State of Washington. They determined that high pH ground water (from caustic brine industrial waste) greatly enhanced arsenic mobility, but mixing with sea water caused precipitation of a number of minerals and reduced permeability along the shoreline. Carillo and Drever (1998) found that significant levels of iron oxides present in the natural aquifer material caused some retention of arsenic in a heavily mined area.

Because it is clear that different environmental conditions strongly influence the level and speciation of arsenic present in contaminated ground water, any practical method for the removal of arsenic should be robust. The current technologies most commonly considered for reduction or removal of arsenic in drinking water are coagulation/filtration (CF) and ion exchange (IE) (EPA/600/R-98/042). Both of these technologies have been shown to reduce arsenic to 2 ppb. They are more effective when arsenic is in the form of As(V). If As(III) is present, it must be oxidized to As(V), necessitating a form of

pretreatment and adding to the overall cost. CF is most efficient at mid-range pH. The efficiency of the process depends on the type of coagulant, resident time, and the dosage range. Disposal of arsenic-contaminated sludge is also a factor in the cost. This is not an appropriate choice for small, rural systems such as the Rosebud Indian Reservation in Todd County (one of the most impoverished county in the United States) because of the high cost, need for well-trained operators, and difficulties of maintaining optimum operating conditions. Ion exchange efficiency is affected by competition with sulfate, selenium, fluoride, nitrate, and total dissolved solids. Suspended solids and iron precipitation can clog the column. Eventually the column must be regenerated with brine. Although this technology is considered appropriate for small ground-water systems (<10,000 users), it is still too costly for water supply systems such as on the Rosebud Indian Reservation, which is located in the poorest county in the United States. Other processes, which are generally less effective than CF and IE, are reverse osmosis, activated alumina adsorption, and lime softening.

B. Aquifer Characteristics

Elevated levels of arsenic on the Rosebud Indian Reservation in the Grass Mountain area, as shown on Figure 1, were first observed in 1990. Levels of arsenic greater than 80 ppb were measured at two production wells in the area. Local residents were provided with an alternate water supply in 1993. The Grass Mountain area is adjacent to the Little White River. Most of the land in this area is utilized for livestock grazing. A study by the United States Geological Survey (Carter et al., 1997) extensively characterized the extent of arsenic in the study area and attributed the primary source of arsenic to be arsenic-rich volcanic ash, which is abundant in the Arikaree Formation and White River Group in South Dakota. The Little White River, a perennial stream with an average discharge of $3.1 \text{ m}^3/\text{s}$, flows to the north. Ground water flows toward the Little White River, with measurable amounts of streamflow gains through the study area. There are also several ephemeral springs in the area.

The recharge area of the High Plains (Arikaree and Ogallala) aquifer is exposed on part of the Rosebud Indian Reservation in south-central South Dakota. The Arikaree Formation is mainly fine-grained, semi-consolidated sand of Miocene age. The material is primarily quartz sand, with some calcareous cement in the deeper part of the formation. Volcanic ash overlies the Arikaree Formation and also is interbedded with sand and silt of the Arikaree; this volcanic ash is a suspected source of arsenic in the ground water. Numerous Arikaree wells exist on the reservation, including community supplies and domestic or stock wells. The Arikaree aquifer is generally unconfined on the Rosebud Indian Reservation, and wells typically are less than 200 feet deep. A potentiometric map of the area is shown on Figure 2.

In contrast to the Arikaree aquifer, the Madison aquifer consists of carbonate rock, primarily limestone and dolomite (Gries and Martin, 1981). The formation is fractured and is karstic where dissolution of the carbonate rock has developed features such as caves and sinkholes. The Madison aquifer's recharge area is exposed on the flanks of the Black Hills, and the ground-water system receives recharge from precipitation on the

outcrop as well as from stream flow losses. Sources of arsenic are primarily from mining regions where arsenopyrite-rich rocks have been exposed. Arsenic and its association with iron hydroxides produced from acid mine drainage are of particular concern. For comparison to the Arikaree aquifer, arsenic transport in the Madison aquifer has been characterized downgradient from swallow holes where Bear Butte Creek sinks into the Madison Limestone. Arsenic concentrations in Bear Butte Creek are well documented from past studies (Davis, Webb, and Durkin, 1999). Arsenopyrite mineralization is associated with the ores in the watershed. This appears to be the major source of arsenic in surface water, ground water, and stream sediments in the basin. Concentrations measured in downgradient wells have been compared to stream samples for a gross indication of adsorptive capacity in a field setting. This information will be compared to arsenic transport in the Arikaree aquifer, where much less adsorption is expected because of the Arikaree's quartz sand and relative lack of carbonate minerals.

C. Relationship to On-Going Work

Previous and on-going work has demonstrated the potential effectiveness of this remediation technology for reduction of arsenic in ground and surface waters to below 10 ppb (Webb and Davis, 1999; Webb, 1999). This has resulted in a better understanding of the physical and chemical processes that govern arsenic retention and transport in ground water and surface water in the Madison Limestone aquifer. Previous work is described in detail in Section 13 of this proposal. This proposed research will build on that work by providing critical information about the maximum adsorptive capacity, influence of surface area, effect of pH, and related factors.

Methods, Procedures, and Facilities

This project will use batch, column, and adsorption tests to evaluate the adsorptive capacity of limestone for arsenic uptake as a function of the level of dissolved arsenic to be remediated as well as the surface area and particle size of the crushed limestone. The optimum conditions for arsenic adsorption and retention in order to reduce arsenic levels below drinking water standards will be determined by the results of the laboratory studies. This proposed research also will concentrate on the total adsorptive capacity of limestone by determining the breakthrough of arsenic from column leaching. In related research work for which additional funding is being sought, it is planned that the process will be scaled up to assess construction and engineering constraints and to determine whether it is feasible in the field.

As mentioned earlier, the specific objectives of this work are to: (1) establish the maximum capacity of limestone to retain arsenic, (2) determine the effect of pH and surface area on adsorption efficiency, and (3) compare arsenic retention on limestone with other materials such as Arikaree sandstone and pure CaCO_3 . Methods to achieve this are described below.

To establish the maximum capacity of limestone to retain arsenic, three-foot columns will be filled with finely crushed limestone. The total mass of limestone will be measured.

The column will be flushed and backfilled with ground water from the Madison aquifer. Madison aquifer water will be introduced at a selected rate until water quality measurements such as pH, conductivity, dissolved oxygen, and temperature from water removed from the column have stabilized. Water samples will be analyzed to determine column background levels of arsenic and other selected analytes. The minimal residence time of analytes in the column will be established with the use of a conservative tracer such as nitrate. In contrast to arsenic, nitrate will exhibit no retention by the limestone and will travel quickly through the column. A nitrate sample with known concentration will be introduced at the top of the column and allowed to equilibrate for 12 hours. Aquifer water will be introduced at a selected rate over a period of days. Output of the column will be monitored until >99% of the nitrate has been removed.

A test with arsenic then will be conducted. An arsenic sample of known concentration will be introduced at the top of the column and allowed to equilibrate with the column for 12 hours. Aquifer water will then be introduced at a selected rate for 24 hours. Leachate samples will be collected and analyzed for arsenic. Additional arsenic of a known concentration will be introduced at the top of the column and allowed to equilibrate for 12 hours. The process will be repeated until arsenic levels in the leachate approach the input concentration, indicating that no further significant arsenic adsorption is taking place. Water will continue to be introduced at a selected rate until water quality measurements have stabilized. Arsenic retention will be evaluated as a function of mass of limestone to establish the breakthrough point of arsenic loading.

To establish the impacts of surface area and pH on arsenic retention, adsorption batch tests will be performed. Bottles will be filled with crushed limestone material and aquifer water containing 100 ppb arsenic with a known mass ratio of limestone to water. The bottles will be shaken continuously for a period of one week. Dissolved arsenic will be analyzed. Batch experiments will be conducted with different grain sizes. Surface area of the limestone will be estimated from the grain size and from N₂ BET (Brunauer, Emmet, and Teller) measurements (Daniels and Alberty, 1961). Batch experiments will be conducted with varying limestone/water mass ratios. This will help establish the maximum retention capacity. Adsorption isotherm curves will be produced. The pH will be measured at the beginning and end of each batch test. The pH of the initial arsenic solution will be varied to determine its effects on adsorption efficiency.

To compare arsenic retention on limestone with other materials such as Arikaree sandstone and pure CaCO₃, companion column and batch tests with the materials will be conducted. Procedures similar to those described with limestone will be followed.

South Dakota School of Mines and Technology has all necessary analytical and biological facilities and the sampling equipment necessary for the successful completion of this project. Graphite furnace atomic absorption spectroscopy will be used to perform analysis of arsenic. During this project, the primary focus will be on the geochemical laboratory investigations. This is necessary to establish conditions for bench-scale and field-scale investigations that are anticipated to take place in the future. Recently, the Western Dakota Water Development District provided a modest amount of startup

funding (\$7500) for work related to project. Arsenic reduction from 100 ppb to 10 ppb was clearly demonstrated with limestone material.

Related Research

This proposed work is part of a larger, on-going program investigating a practical means of reduction of arsenic concentrations in ground water, as mentioned earlier. The principal investigators have determined, from the preliminary results of related research, that more than 90% of the arsenic in ground-water samples can be adsorbed onto limestone (Webb and Davis, 1999; Webb, 1999). Results of other research are presented in the references cited below.

A. Preliminary Results

Laboratory tests were used to characterize arsenic retention in the Madison Limestone and to help establish the optimum conditions for efficient retention. Two grain sizes of crushed material were used in both the column and batch experiments: fine-grained material – 0.055 to 0.234 inches and coarse – 0.187 to 0.234 inches.

i. Batch experiments:

Four batch tests using 0.5-L round bottom flask were conducted using both fine and coarse crushed limestone. Each bottle initially began with 100 mL of ~100 ppb arsenic and varying levels of limestone: 1 gram, 10 grams, 20 grams (sample and duplicate), 50 grams and 100 grams. Additionally a blank sample with 100 mL of deionized water and 20 grams of limestone was analyzed.

The bottles were shaken continuously for a period of three to seven days. Dissolved arsenic was measured. Batch experiments were conducted with different starting pH values for the initial arsenic solution. These experiments helped establish reproducibility of the data as well as characterizing the impacts of surface area on arsenic retention. Adsorption isotherm curves were established as a function of arsenic concentration and mass of limestone. Figure 4 shows the results of one such experiment with fine-grained limestone. Arsenic concentrations dropped from ~100 ppb to less than 10 ppb with a final adsorption of 95%.

ii. Column experiments:

Two three-foot columns were filled with crushed (fine and coarse) Madison Limestone material (~5000 g). The columns were flushed and saturated with distilled water. A conservative tracer test using sodium nitrate was then conducted. A 250 mL sample of 100 ppm nitrate sample was introduced at the top of the column. Water was introduced into the column in 500 mL aliquots. Output of the column was monitored until >99% of the nitrate had been removed.

A corresponding test with a 250 mL sample of ~100 ppb arsenic was then conducted. Madison aquifer water was introduced at a selected rate of 500 mL aliquots. Arsenic retention was evaluated with respect to the tracer experiment. Results of the column experiment, which used fine-grained bed material, are shown on Figure 5.

iii. Summary of previous work:

- a) In all batch experiments, the level of dissolved arsenic dropped from about 100 ppb arsenic to below 10 ppb clearly demonstrating the retention and adsorption of arsenic by the Madison Limestone material.
- b) In each column experiment, arsenic was significantly retained. The column filled with coarse material appeared to retain approximately 75% of the arsenic, whereas the column filled with the fine material retained 100% of the arsenic.
- c) The potential effectiveness of using limestone to reduce arsenic in drinking water to less than 10 ppb has clearly been demonstrated. It is anticipated the technology could be readily adapted to small rural water supply systems as well as private, domestic, and stock wells.

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